

**AN INVESTIGATION OF METALLIC
CRYSTAL FORMATION ON GLASS
BACKING**

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and
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the requirements for the degree of

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IN
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PREFACE

The project described in this paper was undertaken during the 1956 - 1957 academic year at the United States Naval Postgraduate School, Monterey, California.

The purpose of the project was to study the formation of thin metal films on glass backing. The apparatus used was constructed as a thesis project the previous school year. Several important and necessary modifications, however, were found desirable and were added to the existing system.

To date there is little scientific knowledge which adequately explains the nature of metallic crystal formation on glass backing. A statistical interpretation of what occurs is presented herein, and a brief discussion of the observable results obtained is also included. It is hoped that this apparatus and these observations may aid future researchers in an attempt to explain more fully the phenomena investigated.

It is the desire of the writers to express their appreciation for the aid and advice given by Professor Eugene C. Crittenden, Jr. of the Physics Department of the United States Naval Postgraduate School.

Also, the writers wish to thank Mr. M. K. Andrews, Mr. K. C. Smith, and Chief Petty Officer R. C. Moeller for their assistance in obtaining tools and materials and for their advice on various fabrication techniques.

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TABLE OF SYMBOLS AND ABBREVIATIONS

(Listed in the order of their use in the text)

$^{\circ}\text{C}$	- Degrees Centigrade
\AA	- Angstrom Units
IR	- Current Multiplied by Resistance
emf	- Electromotive Force
cm	- Centimeter(s).
v	- Volt(s)
cgs	- Centimeter-Gram-Second System of Units
g	- Gram(s)
amp	- Ampere(s)

CHAPTER I

INTRODUCTION

A field of solid state physics that is drawing increasing attention today is the study of thin films. The literature is filled with papers concerning the properties of thin films of conductors, semiconductors, and insulators. However, one aspect of the subject seems to be relatively unexplored. This is the question of how these films are formed.

The particular studies conducted here involved two metals, cadmium and zinc. This was suggested by Dr. Eugene C. Crittenden, Jr. of the United States Naval Postgraduate School, who had done preliminary work with these materials. He found that it was possible to condense metallic vapor in the form of crystal nuclei or "seeds" on a glass backing cooled to the vicinity of -100°C . The "seeds" could then be grown to a size large enough to be observed with a microscope. This is done by further evaporating more metal and allowing it to strike the glass, after raising the temperature to a higher value, say 0°C . No new nuclei would be formed at this higher temperature. Some type of statistical treatment would have to be developed to account for the physical observations.

Sennett, McLaughlin, and Scott¹ used a method different from the one which will be described here to investigate the formation of cadmium and zinc crystals. They evaporated the metal in the objective chamber of an electron microscope. Crystals were formed at the focus. The interesting point of the whole paper is that no crystals were formed with diameters less

than 200°A.

Equipment especially designed for the work described here was constructed by Wilbarger and Long². However, after a few trial runs, it became apparent that some modifications would be necessary. The system, as modified, is described in Chapters III and IV.

CHAPTER II

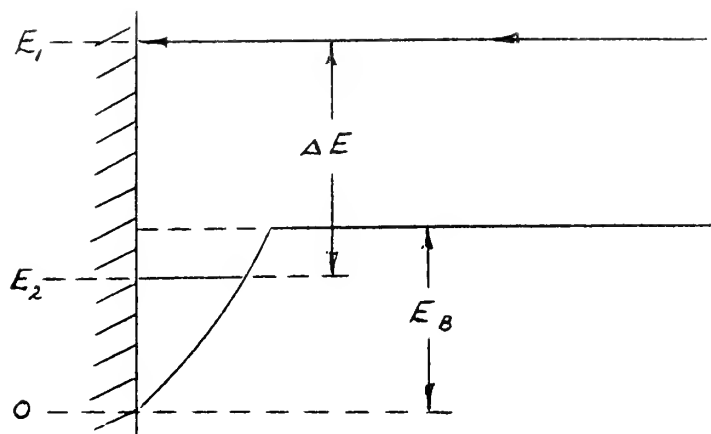
THEORY

There are probably many ways in which the behavior outlined in the introduction may be explained. The problem is to account for the fact that not all atoms striking the cooled surface stick, when the temperature is about -100°C . The model presented here represents one possible means of explaining observed phenomena.

A group of atoms leaving the furnace has a certain mean energy, which is a function of the furnace temperature, less their binding energy. The system is evacuated to a sufficiently low pressure that collisions with air molecules may be neglected.

Upon striking the cooled glass surface, atoms transfer a portion of their kinetic energy to the surface, thus lowering the mean energy of the group. Intermolecular forces between metal atoms and the glass surface present a potential barrier, which atoms must overcome to back-evaporate from the surface. If the mean energy has been lowered sufficiently, the groups of atoms cannot escape from the surface; however, they are still free to move around in the plane of the surface, neglecting intermolecular forces parallel to the plane of the surface.

Figure 1 illustrates the proposed mechanism. Incoming atoms with energy E , lose an amount of energy ΔE ; their energy is then E_2 . If this is less than the barrier height E_B , they cannot escape from the surface; they rapidly transfer their remaining excess energy to the surface, coming to equilibrium with it. Metal atoms on the surface, free to move in the plane of



E_B = binding energy to surface, due to intermolecular forces.

E = kinetic energy loss to surface

FIGURE 1

the surface, may now be considered as a two dimensional gas. If the total number is N , and the area is A , then the number per unit area, n , is given by:

$$n = N/A;$$

and any element of area dA would contain dN atoms,

$$dN = ndA.$$

Here, dA must be much larger than the order of atomic dimensions.

Consider a rectangular coordinate system, with X and Y axes perpendicular. If v_x and v_y represent the X and Y components of velocity, respectively, then the velocity is $v^2 = v_x^2 + v_y^2$; also, all directions of velocity will be equally likely (in the XY plane). Now, considering a coordinate system



in two dimensional velocity space, it is desired to find the fraction of atoms with X components of velocity between v_x and v_x+dv_x ; call this fraction $\frac{dN_{v_x}}{N}$. This quantity is proportional to the magnitude of dv_x and to some function of the velocity. $f(v_x)$:

$$\frac{dN_{v_x}}{N} = f(v_x) dv_x$$

It can be shown that the fraction with velocity components between v_x and v_x+dv_x , and v_y and v_y+dv_y , is given by

$$\frac{d^2 N_{v_x v_y}}{N} = f(v_x)f(v_y)dv_x dv_y$$

It can also be shown that the functions $f(v_x)$ and $f(v_y)$ have the form:

$$f(v_x) = \alpha e^{-\beta^2 v_x^2};$$

$$f(v_y) = \alpha e^{-\beta^2 v_y^2}$$

Therefore,

$$d^2 N_{v_x v_y} = N \alpha^2 e^{-\beta^2 (v_x^2 + v_y^2)} dv_x dv_y, \quad (1)$$

$$\text{or } d^2 N_{v_x v_y} = N \alpha^2 e^{-\beta^2 v^2} dv_x dv_y. \quad (2)$$

The density of points in velocity space is:

$$\frac{d^2 N_{v_x v_y}}{dv_x dv_y} = N \alpha^2 e^{-\beta^2 v^2}, \quad (3)$$

where each point signifies the end of a vector drawn from the origin to represent a particular velocity. The number of atoms with speeds between v and $v+dv$ is the same as the number of points in an annular ring with radii v and $v+dv$. The area (in velocity space) of such a ring is $2\pi v dv$. This, multiplied by

the density of points. gives the number of points:

$$dN_v = 2\pi N \alpha^2 v e^{-\beta^2 v^2} dv. \quad (4)$$

This is the distribution of speeds. To evaluate α in terms of β , integrate the speed distribution function over all possible speeds and equate to the total number of atoms, N:

$$\begin{aligned} N &= 2\pi N \alpha^2 \int_0^\infty v e^{-\beta^2 v^2} dv \\ 1 &= 2\pi \alpha^2 \left[-\frac{e^{-\beta^2 v^2}}{2\beta^2} \right]_0^\infty \\ 1 &= 2\pi \alpha^2 \left(\frac{1}{2\beta^2} \right) \\ \alpha^2 &= \beta^2 / \pi, \text{ OR} \\ \alpha &= \beta / (\pi)^{1/2}. \end{aligned} \quad (5)$$

Putting this in for α in (4), the following is obtained:

$$dN_v = 2N\beta^2 v e^{-\beta^2 v^2} dv \quad (6)$$

The average speed, \bar{v} , is then given by:

$$\begin{aligned} \bar{v} &= \frac{1}{N} \int_0^\infty v dN_v \\ &= \frac{1}{N} \int_0^\infty 2N\beta^2 v^2 e^{-\beta^2 v^2} dv \\ &= 2\beta^2 \int_0^\infty v^2 e^{-\beta^2 v^2} dv \\ &= 2\beta^2 \cdot \frac{1}{4} \cdot \left(\frac{\pi}{\beta^4} \right)^{1/2} \\ \bar{v} &= (\pi)^{1/2} / 2\beta, \text{ AND} \\ \beta &= (\pi)^{1/2} / 2\bar{v}. \end{aligned} \quad (7)$$

The root mean square speed is a useful quantity, and may be obtained as follows:

$$\begin{aligned} v_{rms} &= (\overline{v^2})^{1/2} = \left[\frac{1}{N} \int_0^\infty v^2 dN_v \right]^{1/2} \\ &= \left[2\beta^2 \int_0^\infty v^3 e^{-\beta^2 v^2} dv \right]^{1/2} \\ &= \frac{1}{\beta}. \end{aligned} \quad (8)$$

The most probable speed, v_m , is obtained by differentiating equation (6) after dividing through by dv , and equating to zero:

$$\frac{d}{dv} \left(\frac{dN_v}{dv} \right) = 2N\beta^2 (1 - 2\beta^2 v_m^2) e^{-\beta^2 v_m^2} = 0$$

In order not to have a trivial solution, the quantity in parentheses must equal zero.

$$1 - 2\beta^2 v_m^2 = 0$$

$$v_m^2 = \frac{1}{2\beta^2}$$

$$v_m = \frac{1}{\sqrt{2}\beta} = \frac{v_{rms}}{\sqrt{2}} \quad (9)$$

The kinetic energy of an atom on the surface is $\frac{1}{2}mv^2$. The average energy of a group is $\frac{1}{2}m(\overline{v^2})$ per atom, since the masses are all the same. From the principle of equipartition of energy, \overline{w} , of a particle with f degrees of freedom is given by:

$$\overline{w} = \frac{f}{2} kT,$$

where k = Boltzmann's constant

and T = absolute temperature.

For the two dimensional gas, $f = 2$, so that

$$\frac{1}{2}m(\overline{v^2}) = kT$$

$$(\overline{v^2}) = 2kT/m$$

$$\sqrt{(\overline{v^2})} = v_{rms} = \sqrt{\frac{2kT}{m}}$$

Now, β may be evaluated in terms of m , k , and T :

$$\beta = \frac{1}{v_{rms}} = \sqrt{\frac{m}{2kT}} \quad (10)$$

The speed distribution function (6) now becomes:

$$dN_v = \frac{Nm}{kT} v e^{-\frac{mv^2}{2kT}} dv \quad (11)$$

The distribution of energies may be obtained by putting $w = \frac{1}{2}mv^2$, and noting that $dw = mv dv$. Making these substitutions in (11), and changing to dN_w , the expression becomes:

$$dN_w = \frac{N}{kT} e^{-w/kT} dw \quad (12)$$

From this, it is readily apparent that the probability of observing a particular energy is increased if the temperature is lowered, for energies less than kT . The opposite is true for high energies.

Knowing the distribution of velocities, one may calculate the frequency with which atoms collide on the surface. This may then be correlated with the actual number of crystals obtained on the surface. It is in this way that the model may be tested.

Calculation of collision frequency for a Maxwell distribution is quite difficult. A fair approximation may be obtained by assuming that all atoms are at rest except one. Let it be moving with the velocity \bar{v} . Further assume that all atoms are points except the one that is in motion. Let it have a diameter equal to twice the molecular diameter. An examination of Figure 2 reveals that this fictitious atom will make the same number of collisions with "points" as the original atom would have made with others of the same size. Now in a time t , the atom travels a distance $\bar{v}t$, sweeping out an area $2s\bar{v}t$. If there are n atoms per unit area, the number of collisions is $2ns\bar{v}t$. The collision frequency, p , is then:

$$p = 2ns\bar{v} \quad (13)$$

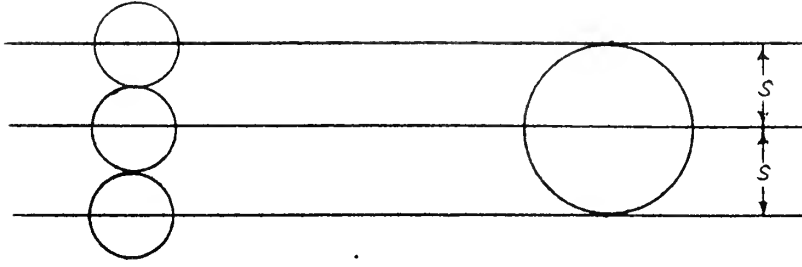


FIGURE 2

In the case of a three dimensional system, Kennard⁴ gives the following expression for collision frequency:

$$p = Sn\bar{v},$$

where S is the collision cross section (equivalent of $2s$ for a two dimensional system). The three dimensional case is also worked out for a Maxwellian distribution. The only difference is that the expression for p must be multiplied by the square root of two. In the two dimensional system, with the Maxwellian velocity distribution, the collision frequency is the same expression given in (13) multiplied by a constant k :

$$p = 2ksn\bar{v}. \tag{14}$$

The numerical value of k may be obtained by methods similar to those given in Kennard⁴.

Let the number of crystal "seeds" formed in a time t be y . This number is obviously proportional to the time of exposure, and to the collision frequency. It is also some function of



the mean energy, which is a function of the temperature; call this function $f_1(T)$, or f_1 . Then,

$$y = pt f_1(T). \quad (15)$$

Now, y and t may be determined experimentally, giving the following:

$$p f_1 = y/t. \quad (16)$$

Let \dot{n} be the rate at which atoms arrive at the surface, per unit area. This quantity can be measured directly; the method is described in Chapter V. Let \dot{n}' be the rate at which atoms are back evaporating from the surface. This is proportional to the number of atoms on the surface:

$$\dot{n}' = f_2(T) n, \quad (17)$$

where $f_2(T)$ is a proportionality factor depending on the temperature. The Clausius-Clapeyron equation could be used to find the form of this dependence, but this is not included here. After equilibrium has been attained, and assuming that the fraction of atoms actually sticking is small, (i.e., assuming that the number removed by the seeds is negligible compared with the total number of atoms), \dot{n}' may be equated to \dot{n} , giving:

$$\dot{n} = f_2 n. \quad (18)$$

From (14) and (16),

$$n = \frac{y/t}{2ksvf_1}. \quad (19)$$

Put this in for n in (19):

$$n = \frac{1}{2Ksv} \cdot \frac{f_2}{f_1} \cdot \frac{y}{t} \cdot \quad (20)$$

If the temperature is held constant over several runs, a plot of n against y/t should yield a straight line. Then the temperature could be varied to study its effect.

This entire discussion has been based on the assumption of complete surface mobility of the atoms. There is quite a good possibility that mobility is limited, i.e., that atoms travel a short distance and come to rest. At the temperature of liquid nitrogen, it is probable that all atoms striking the surface stick immediately. This produces a uniform film, if atoms have restricted mobility. At a temperature of about -100°C. , the degree of mobility is completely unknown; further work should provide evidence to either support or contradict the proposition of complete mobility.

CHAPTER III

THE VACUUM SYSTEM

The apparatus used in this study may be divided into two parts for the purpose of discussion: the vacuum producing system and the working space. These sections are divided by a three-quarter inch general purpose steel base plate upon which a variety of experimental systems requiring a vacuum may be installed. An overall view of the apparatus is shown in Figure 4.

The vacuum producing system consists of a conventional fore pump and diffusion pump. The fore pump is a Kinney compound vacuum pump, Model KC 15, with a theoretical displacement of 7.2 liters per second. The diffusion pump is a four inch fractionating type pump, manufactured by the Consolidated Vacuum Corporation. It has a theoretical displacement of 300 liters per second; however, when installed the displacement probably does not exceed 100 liters per second.

An aluminum adapter plate is bolted to the top of the diffusion pump. Above this is attached a sheet aluminum vapor bafflesystem. The baffles deflect oil vapor particles from the diffusion pump downward, thereby keeping the number entering the working space at a minimum. A four inch quarter-swing vacuum valve is attached just below the general purpose base plate, so that the working space may be sealed off from the pumping system, if desired.

There are two more openings in the base plate, into which are inserted vacuum connectors. In one is a Pirani gauge tube, in the other an ionization gauge tube, VGIA, used for determining



the final vacuum.

In addition, a Stokes McLeod gauge (Flosdorf modification), for measuring pressure at the fore vacuum end of the diffusion pump, is attached to the elbow connection nearest the diffusion pump.

The pumps and connections are shown in Figure 5. The best vacuum achieved to date was 4.8×10^{-7} millimeters of mercury, as measured by the ionization gauge, Type DPA-38, manufactured by the Consolidated Vacuum Corporation.

Figure 6 shows a diagram of the safety interlock circuit built into the system. All switches and relays are normally as shown on the circuit diagram, once the on-switch at (1) is closed. The arrowheads indicate the flow of current through the diffusion pump power circuit. The holdings relays (6) and (7) are closed when the push-button at (5) is depressed. since a surge of current in the coil above the relays creates a magnetic field which closes them as indicated. After the push-button at (5) is released. the relays (6) and (7) remain closed; and the circuit is intact.

The interlock circuit protects the system as follows:

- (a) If the line current fails, the relays at (6) and (7) are opened, thus opening the diffusion pump power circuit. The relay at (7) makes contact so as to light the alarm lamp located on the control board of the system. Until the push-button at (5) is manually depressed, the diffusion pump can't start up again. This keeps the diffusion pump from starting if the line current is restored while the fore pump is still off.

- (b) Should the diffusion pump become overheated, a thermal switch will open the circuit where shown. Therefore, the relays at (6) and (7) are opened, the alarm lamp is lit, and the diffusion pump is shut off, not to be started until the push-button (5) is once again closed.
- (c) In the event of a failure of the high vacuum recorded on the ionization gauge, an internal relay in the ionization gauge energizes the coil shown, which opens the relay at (2). The circuit is thus opened, and the same effect as described in (a) and (b) is observed.
- (d) Should there be a major vacuum failure, e.g., "implosion" of one of the pyrex beakers mounted in the top plate, the sudden increase in pressure will close the pressure operated microswitch in (8), which in turn will energize the coil that opens the relays at (3) and (4). Thus the diffusion pump and fore pump are both turned off, to be started again only by manual operation. The microswitch (8) is located between the diffusion pump and fore pump. Perhaps a better location would be a connection into the working space itself.

CHAPTER IV

THE WORKING SPACE

The confines of the vacuum in the working space are the steel base plate mentioned in Chapter III. a 14 inch diameter glass cylinder about 17 inches high, and an aluminum top plate into which are inserted two pyrex beakers. Resting on the top plate is a liquid nitrogen trap, which has coils extending into a charcoal trap within the vacuum. Above the top plate a mixer, fitted to a plastic stirring rod, is used to stir the contents of one of the beakers. Various electrical leads are inserted in both the top and base plates. All electrical wiring and relays are consolidated behind the panel which may be observed in Figure 4, the overall view of the apparatus. A descriptive discussion of the various components of the working space and their operation follows:

1. The Base Plate.

Figure 7 is a photograph of the base plate. In the middle may be observed a copper shield over the pumping orifice; this prevents any small particles from falling into the diffusion pump.

On either side of the shield are two tungsten wire filaments on which are wrapped several turns of #27 bare copper wire. When a current is passed through the tungsten wire, it heats up; and the copper is evaporated all over the interior of the glass cylinder. The purpose of this is to trap scattered zinc or cadmium atoms evaporated from the main furnace, since it is known that zinc or cadmium will stick to a freshly ;

coated copper surface.

Just above the shield is the main furnace, supported by two steel rods. It consists of an alundum cement coated spiral of tungsten wire which contains the metal to be evaporated. The control circuit is shown in Figure 3. The two variacs in series enable one to make a fine adjustment, and the ammeter and voltmeter permit duplication of the rate of evaporation on successive runs.

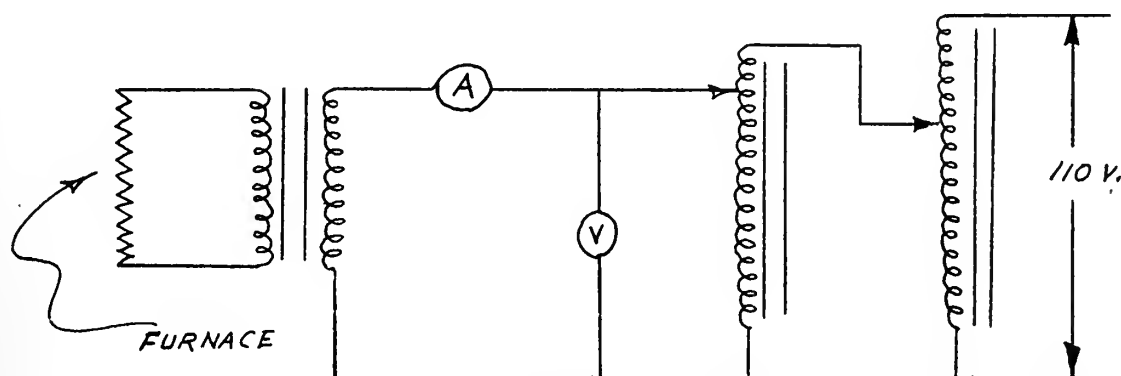
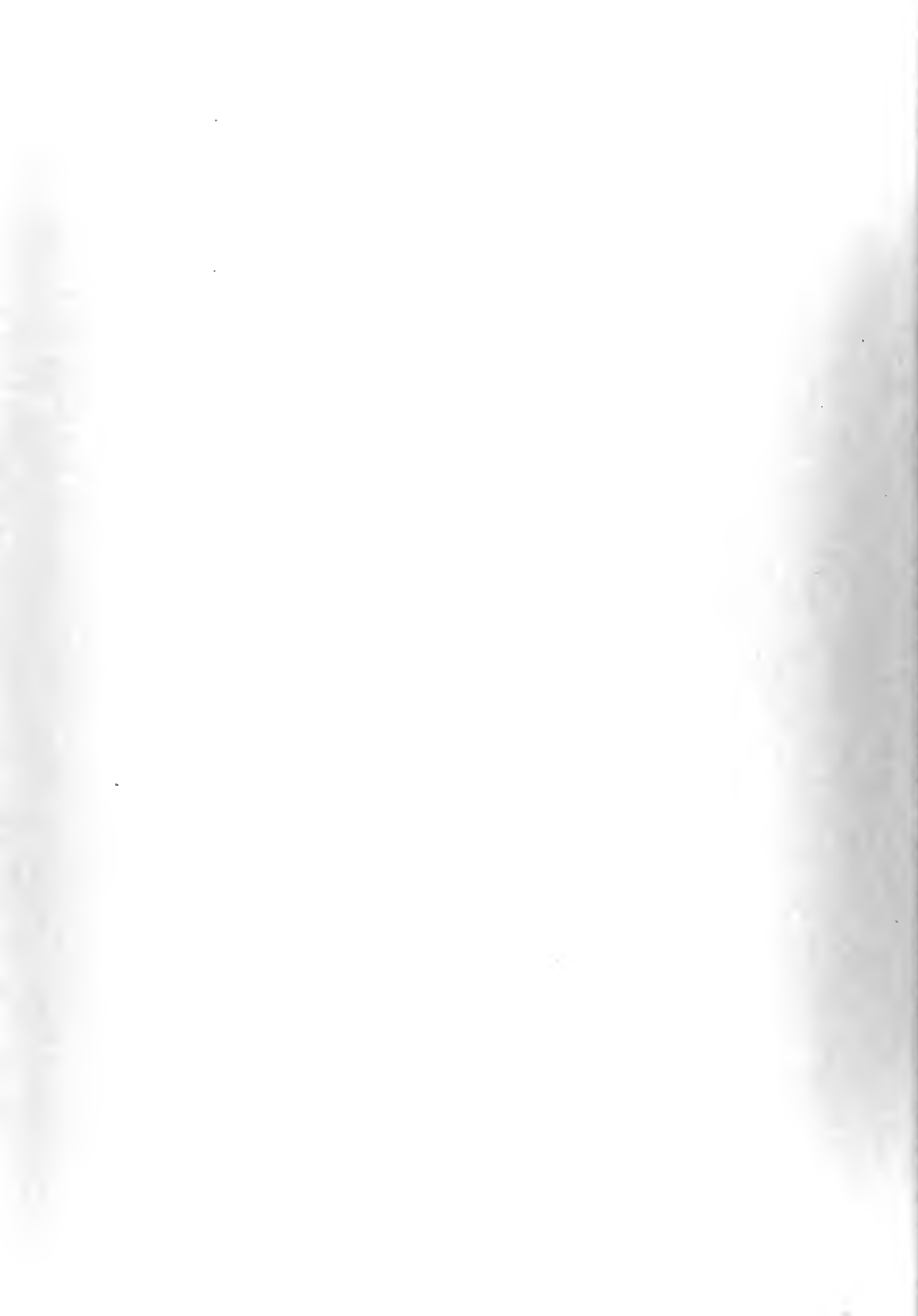


FIGURE 3

Toward the rear of Figure 7 may be observed two pointed brass rods seated in the base plate approximately eight inches apart. These extend to the top plate when the apparatus is assembled; and when they are lined up with two marks on the bottom of the top plate, they serve to assure the same geometrical configuration of the system each time a run is made.

2. The Top Plate.

The top plate is made of aluminum; it is one inch thick and 20 inches in diameter. It supports within the vacuum two beakers, a shutter device, a charcoal trap, and various electrical leads. These components will be discussed separately.



A photograph of these items is shown in Figure 8. On top of the top plate is a liquid nitrogen reservoir. the functions of which will be made apparent later.

3. The Charcoal Trap.

A cylindrical copper can, open at the top and bottom, enclosing a helix of $\frac{1}{2}$ inch copper refrigeration tubing connected to the liquid nitrogen reservoir above the top plate, makes up the charcoal trap. Between the coils of the copper tubing is tungsten wire insulated with porcelain fishspine beads to be used as a heater coil. Also, on the inside of the tubing is a cylindrical copper screen. Charcoal may be packed between the screen and the can to make this a true charcoal trap. However, it was found that the vacuum obtained was the same whether charcoal was used or not. Therefore it was decided to leave out the charcoal to eliminate the time-consuming degassing which would be necessary each time.

The usefulness of the charcoal trap is threefold: (1) The tungsten wire heater coil degasses all the components of the trap while a vacuum is being obtained. (2) A copper shield is attached by a metal strap to the cylindrical copper can. This shield is supported just above the main furnace when the system is in operation. The purpose of the shield is to capture extraneous zinc or cadmium atoms and to permit passage of those which are going toward the beakers. (3) The liquid nitrogen in the copper coils cools all parts of the trap and shield, thereby increasing their ability to capture extraneous zinc or cadmium. Furthermore, any oil vapor that escapes from the diffusion pump will be trapped also.



4. The Beakers.

Two 250 cubic centimeter pyrex spoutless beakers are supported from the top plate. The vacuum seal is accomplished by use of 1/16 inch rubber gaskets around the lips of the beakers and thin rubber rings which are clamped down on top of the beakers by steel rings. One beaker is for the collection of the specimen to be studied: the specimen beaker; the other is for the measurement of the rate at which the metallic vapor strikes the beakers: the rate recording beaker. The relative positions of the beakers may be observed in Figure 8; the specimen beaker is one the left.

The rate recording beaker is provided with four painted silver electrodes; Hanovia silver paste #38 was used. Leads, soldered to these electrodes, run to electrical leads in the top plate. These electrical leads, in turn, are connected to a recording system on the outside. The principle involved in measuring the rate of evaporation of the metallic vapor is to measure the rate of rise in the conductivity of a thin strip of metal being deposited across the electrodes on the beaker. In the course of a run this beaker is partially filled with liquid nitrogen to assure that the metal will stick to the glass and that a constant temperature is maintained. A glass shield, made by cutting the bottom three inches from another of the beakers, is placed around the recording beaker to keep scattered particles from plating around its sides and disrupting the recording mechanism. Figure 9, at the right, shows the appearance of the rate recording beaker after a run has been completed.

The circuit used to record the rate of rise of conductivity is shown in Figure 10. The requirements of the circuit are to provide a current through the strip directly proportional to the conductivity of the strip in such a manner that the effect of contact resistance at all four contacts is eliminated. The output of the self-balancing potentiometer, General Electric, catalog number 8901490G2, is governed by the IR drop across the probes (R_1 and R_2), which is matched by the emf of the Rubicon potentiometer, approximately 50 millivolts. As more metal is plated out, the IR drop across the probes decreases, throwing the circuit out of balance; the self-balancing potentiometer corrects this by increasing the current through the strip. The circuit is sensitive enough so that this increase in current, as plotted on the Esterline-Angus recorder, is a smooth curve. The slope of this curve is proportional to the rate of deposit of metal on the beakers.

The specimen beaker must meet two requirements: (1) it must be maintained at a known temperature for the duration of the first exposure; (2) it must provide a flat, uniform surface upon which the specimen is to be collected. It was discovered, upon investigation beneath a microscope, that the surface of the beaker itself did not meet the stringencies of the latter requirement. Therefore, a cut portion of a microscope slide was glued to the bottom of the beaker with commercial silicate of soda solution. This may be observed on the left in the photograph, Figure 9.

To prevent scattered particles from impinging on all parts of the beaker, a cut beaker was used in the same manner as de-

scribed for the rate recording beaker above. However, this method was discarded after a time due to back scattering and reflection of the particles from the metal shield in the shutter assembly just below the beaker. The final arrangement was as is shown beneath the beaker on the left in the photograph, Figure 8. A $\frac{1}{4}$ inch thick flat piece of glass with a hole in the center, through which extends a length of $\frac{1}{2}$ inch outside diameter glass tubing, lies snugly against the microscope slide which is glued to the bottom of the beaker. The piece of glass tubing is glued to the glass plate with sodium silicate and protrudes through the hole in the metal shield beneath the beaker. A helical spring around the glass tube between the shield and beaker keeps the glass plate fitting tightly against the microscope slide. This arrangement prevents back-scattering from the metal shield and almost negates extraneous effects due to scattered metal particles striking that portion of the specimen beaker that is to be studied.

The requirement of temperature control involves two major problems. One is attaining and keeping a uniform temperature throughout the beaker; the other is knowing exactly what this temperature is. In order to maintain an equilibrium temperature, a quantity of 2-methylbutane (freezing point = $-155^{\circ}\text{C}.$) is introduced into the beaker. A length of copper tubing from the liquid nitrogen reservoir is coiled throughout the interior of the beaker to cool the 2-methylbutane. A needle valve at the top controls the flow of liquid nitrogen through the tube. To assure uniformity of temperature throughout the bottom of the beaker, the contents are kept in constant agitation by a plastic

stirring rod rotated by an ordinary household mixer motor.

Measurement of the temperature is accomplished by means of an iron-constantan thermocouple, with reference temperature of 0°C . The temperature is read on a Minneapolis Honeywell Brown ElectroniK recorder, shown in Figure 11, which was calibrated as follows:

1. Handbook values of emf versus temperature in the range 0°C . to -200°C . were plotted on the line marked \odot shown in Figure 12.
2. Equilibrium freezing mixtures of several substances, e.g., ethyl acetate, were prepared, so that measured emf's could be compared with known temperatures. The determinations were plotted as the points \triangle in Figure 12.
3. The deviations between the above two curves were applied to a variable correction ranging from 0 millivolts at -80°C . to $+.23$ millivolts at -200°C . These corrected points were plotted at every 5°C . as \square in Figure 12, and a smooth curve was drawn.
4. It was determined that the working range would be from -60°C ., which corresponds to -3.0 millivolts, to -140°C ., which corresponds to -6.3 millivolts. Therefore, the span of the recorder scale was found to be 3.3 millivolts. The ratio of the length of the scale on the recorder to the distance from -6.3 to -3.0 millivolts on the graph was applied to the graph distances, and the corresponding temperatures were properly entered on the recorder scale.

5. Finally the recorder was calibrated with a potentiometer. (This was done, incidentally, just before each run.).

5. The Shutter System.

Just below the bottoms of the beakers as shown in Figure 8 is a system of shutters, which control the time during which the collecting surfaces are exposed to the metal source. The shutters consist of 1/16 inch thick brass plates which are soldered to brass shafts. An arm is fastened to the end of each shaft; to these arms are attached some fine resistance wires. When these wires are attached also to the rods projecting downward from the top plate, the shutters are held in a cocked position and may be tripped electrically by burning out the wire.

Copper shields are mounted on either side of the two beakers so that metal particles from the melting resistance wire cannot contaminate the beaker surfaces.

There is just one shutter beneath the rate recording beaker, on the right, in Figure 8. This is opened at the start of a run and remains open throughout.

Beneath the specimen beaker are three shutters; one opens and exposes the specimen surface after a proper rate of evaporation of metal has been established; after a predetermined time has elapsed, a second closes and shields the specimen surface to permit raising its temperature; finally, when the specimen surface has warmed to a new isothermal temperature, a third shutter once again exposes it so that crystal growth may begin. When crystal growth is to be stopped, the furnace power is shut off.

CHAPTER V

FUNCTIONING AND CALIBRATION OF THE RATE RECORDING CIRCUIT

It was desired to measure the exact rate at which atoms of zinc or cadmium arrive at the surface upon which they are to be deposited. Details of the apparatus and electrical circuit were discussed in Chapter IV. A plot of the current through the metal strip as a function of time is produced by the Esterline-Angus recorder. The circuit is arranged so that this current, I , is proportional to the conductivity, C ; or, as expressed by Ohm's Law,

$$I = CE,$$

where E is the potential maintained by the Rubicon potentiometer. A diagram of the circuit is shown in Figure 10.

Conductivity may be expressed in terms of the cross sectional area, A , length, l (between the probes R_1 and R_2), and the resistivity, r , of the strip of metal:

$$C = A/rl.$$

The cross sectional area is variable and increases as more metal is plated out. The width, w , is fixed by the dimensions of the slit through which metal vapor must pass. The thickness, h , is then the only quantity which varies with time, t . By substituting for C in Ohm's Law, with $A(t) = wh(t)$, and solving for $h(t)$, one obtains

$$h(t) = rl/wE \times I(t).$$

Let n be the number of atoms of metal per unit area on the surface. The mass per unit surface area is then nM/N' , where M is the molecular weight and N' is Avogadro's number. The mass

per unit area may also be expressed by Dh , where D is the density. Equating these two expressions for mass per unit area and solving for n yields:

$$n = DN'h/M.$$

Substitution for h from above gives:

$$n = rIDN'/wEM \times I(t).$$

The rate at which atoms strike the surface, dn/dt , is then given by:

$$dn/dt = rIDN'/wEM \times dI/dt = K \times dI/dt,$$

where K is equal to the group of constants.

Table I lists the value of each constant and its source.

TABLE I

<u>Constant</u>	<u>Metal</u>	<u>Value</u>	<u>Source</u>
l	-	2.00 cm.	Measurement
w	-	0.60 cm.	Measurement
E	-	0.050 v.	Measurement*
N'	-	6.02×10^{23} (cgs)	Handbook**
D	Cd	9.16 g/cm^3	Metals Reference Book***
M	Cd	112.41	Handbook**
r	Cd	1.80 ohm-cm.	Handbook**
D	Zn	7.50 g/cm^3	Metals Reference Book***
M	Zn	65.38	Handbook**
r	Zn	1.42 ohm-cm.	Handbook**

* Rubicon potentiometer was set to maintain the desired value.

** Handbook of Chemistry and Physics, 35th Edition.

*** Metals Reference Book, Second Edition, Volume Two.

The following values for K were calculated:

for cadmium, $K = 5.87 \times 10^{24}$ atoms/cm² amp

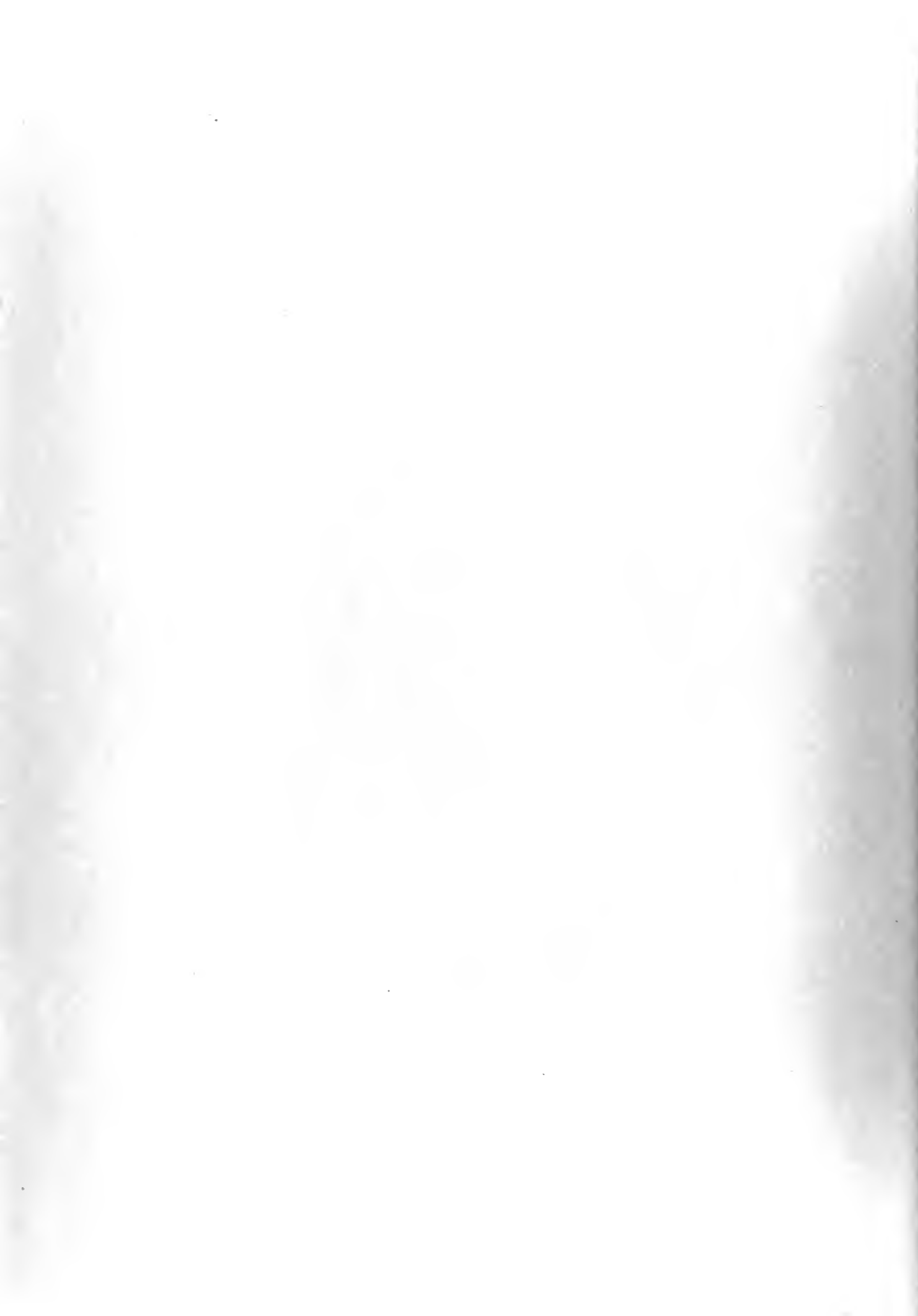
for zinc; $K = 6.52 \times 10^{24}$ atoms/cm² amp

The rate, dn/dt , is obtained by measuring the slope of the plot made by the recorder, and multiplying this by the appropriate K. The accuracy of this determination depends primarily on the validity of assuming that a thin strip of metal has the same properties as a thick strip, that is, whether tabular values of D and r apply to a thin strip. Since the evaporation is carried out at a pressure of about 1×10^{-6} millimeters of mercury, or less, interference by gas molecules should be slight. At the rates of evaporation used for most runs, the strip soon becomes fairly thick (several thousand Angstrom units); therefore, it is felt that values of K are as accurate as need be here.

There is, however, another factor which must be considered. The value of K is used to determine the rate for the recording beaker. This rate is assumed to be the same for the specimen beaker, from the geometry of the system. An attempt was made to check this by depositing metal on the specimen beaker at liquid nitrogen temperature. The deposit was then dissolved in hydrochloric acid and made alkaline with ammonium hydroxide. Two milliliters of 5% resorcinol solution (in absolute alcohol) were then added, and the volume was adjusted to 100 milliliters. Upon standing, the solution developed a blue color. A Beckman Model DU Spectrophotometer was used to measure the percentage transmission of light of wavelength 6200 Å through this solution. The value obtained was compared with a series of standards, prepared from solutions of known concentrations. Concentration was



plotted versus percentage transmission; see Figure 13. From this curve, the unknown concentration was found, and the total weight of metal calculated. This was easily converted to the number of atoms striking the surface per square centimeter per second. This value was quite different from the one obtained by using the K equation above. The system was modified in an attempt to correct the geometry, so that better agreement could be obtained.



CHAPTER VI

OBSERVATIONS AND CONCLUSIONS

It was necessary to count the number of "seed crystals" formed on the specimen surface for each run made. Since the crystals were microscopic in size, it was convenient to use a microscope with a camera attachment, in order that a permanent record could be obtained. The apparatus is shown in Figure 14.

The microscope is of a type designed for metallurgical uses, with an arrangement for vertical illumination. Controls for light intensity and focus are provided; various filters may also be used. The camera attachment is fastened to the barrel, after removal of the eyepiece. An image is obtained on the ground glass screen by adjusting the microscope focussing knob and the light intensity and focus controls. A film plate is inserted in the camera, the proper time is set on the shutter speed knob, and the exposure is made. A mounting plate for holding the specimen surface in a level position is shown on the microscope stage. Leveling is accomplished by adjustment of the three screws which serve as legs. The specimen is secured to the mounting plate with "tacking wax".

Figure 15 shows a specimen obtained prior to the use of microscope slides cemented to the bottoms of the beakers. Poor focussing is due to the unevenness of the surface. In this run zinc was evaporated and a complete metal film was obtained; the edge may be seen across the upper left hand corner of the picture. Some small individual crystals were obtained adjacent to the film, due to diffusion of atoms outward from the area of



direct exposure. The temperature was -89.5°C . for this run. In subsequent runs, an attempt was made to reduce the second exposure to a point where individual crystals would be large enough to see, but would not have grown together to form a film.

Figure 16 shows a specimen obtained using cadmium. Many small seeds and a few large ones are visible. Greater magnification gave the picture shown in Figure 17. The temperature was -101°C ; the time for the first exposure was 75 seconds.

A similar run was made after modifying the system slightly. A glass shield was placed so that no back-scattering from the shutter assembly could affect the collecting surface. The temperature was -98.6°C ; exposure time was 120 seconds. The result is shown in Figure 18. Seeds have grown together to give a semi-opaque film. Individual seeds may still be discerned in the film, however. Figures 19 and 20 were taken at the edge of the film. Here individual crystals may be seen; diameters are of the order of one micron. The area shown in Figure 21 is adjacent to that of Figure 19, overlapping to some extent and a bit farther away from the film. The density of atoms appears not exactly uniform; this is probably due to the geometry of the system. However, the number of seeds per unit area in Figure 21, which is outside the film, is nearly the same as that in Figure 18, which is within the film. This uneven effect was much more pronounced in previous runs, but some adjustment is still necessary to get the desired data.

Before the addition of a shield to prevent scattering from the shutter assembly, pictures such as Figure 22 were obtained



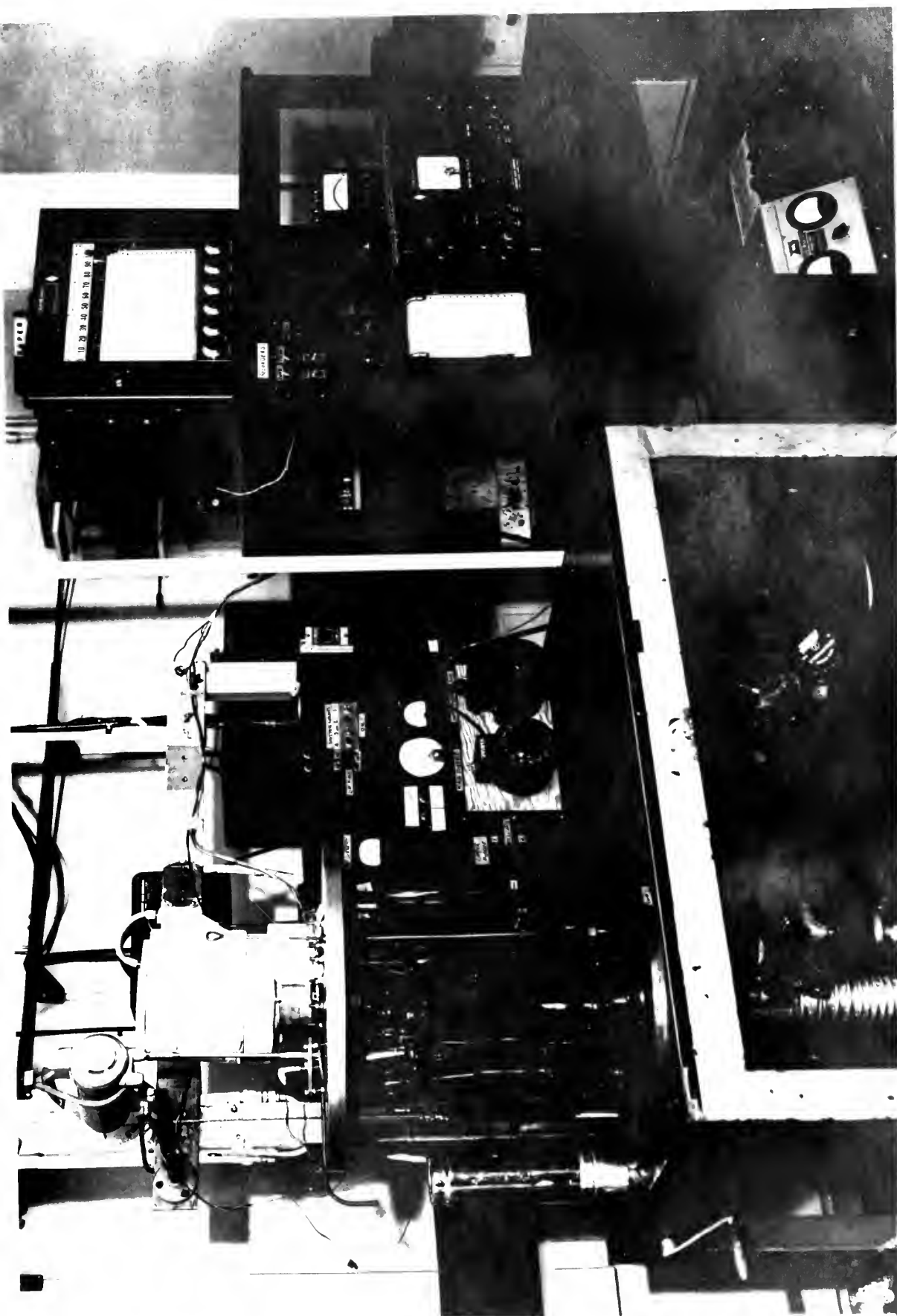
at points on the specimen surface out of direct line with the furnace. There is a large central mass surrounded by many small seeds. The large mass apparantly acted as some kind of scattering center. Its diameter is about ten microns. The number of seeds diminished farther out, and none were visible beyond about 50 microns.

Enough data to test equation (20) in Chapter II could not be obtained, but results do suggest that the proposed model may be valid. An examination of data obtained led to the following conclusions:

1. At temperatures near -100°C. , only a very small fraction of atoms striking the surface stick to it.
2. Individual crystals having diameters of the order of one micron may be formed on the surface.
3. These crystals are grown from "seeds" initially containing a few atoms, probably only two.

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3. F. W. Sears, *Thermodynamics*, Second Edition, Chapter 12, Addison-Wesley, 1953.
4. E. H. Kennard, *Kinetic Theory of Gases*, First Edition, Chapter III, McGraw Hill, 1938.



OVERALL VIEW OF APPARATUS
FIGURE 4

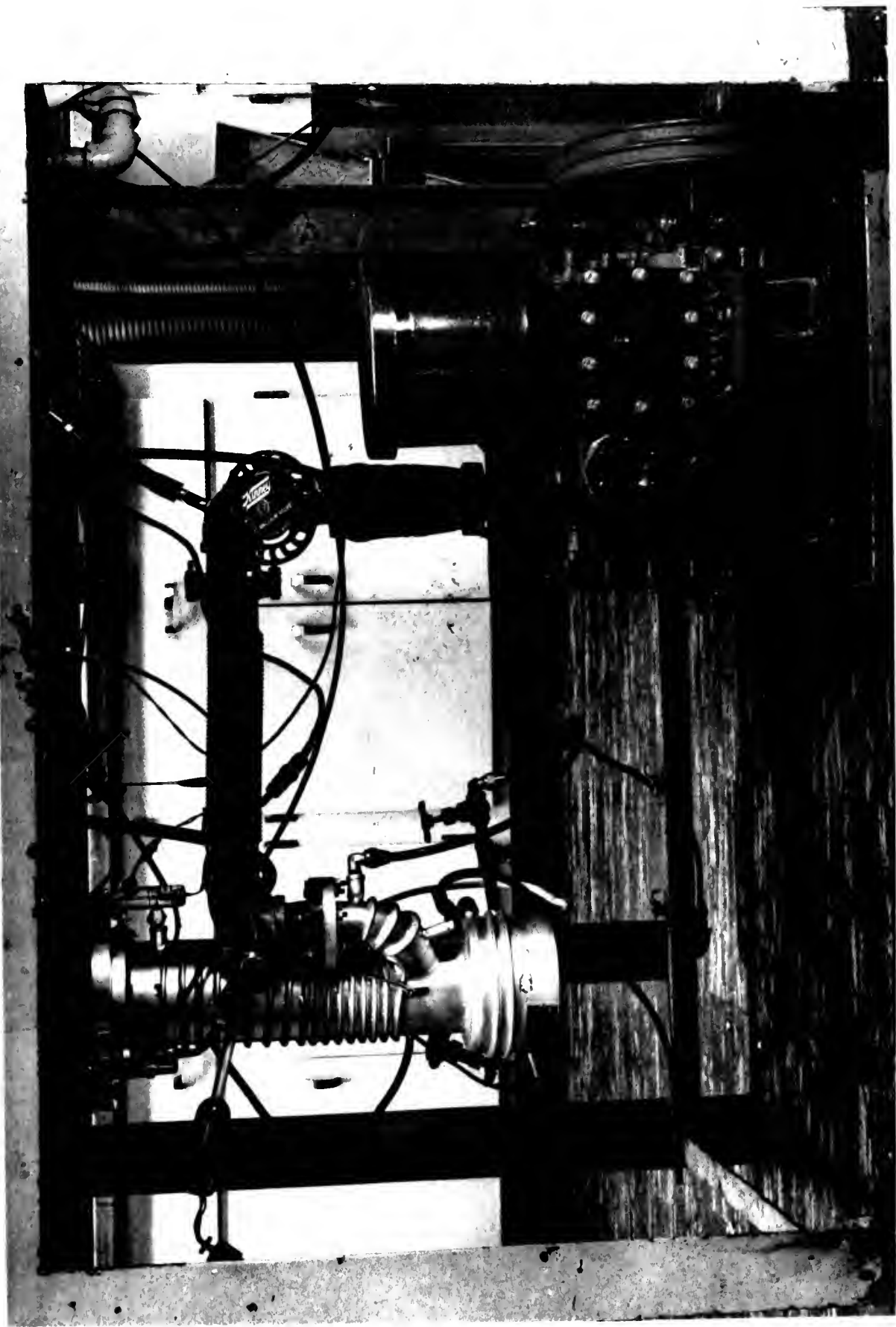


FIGURE 5
THE VACUUM PUMPS

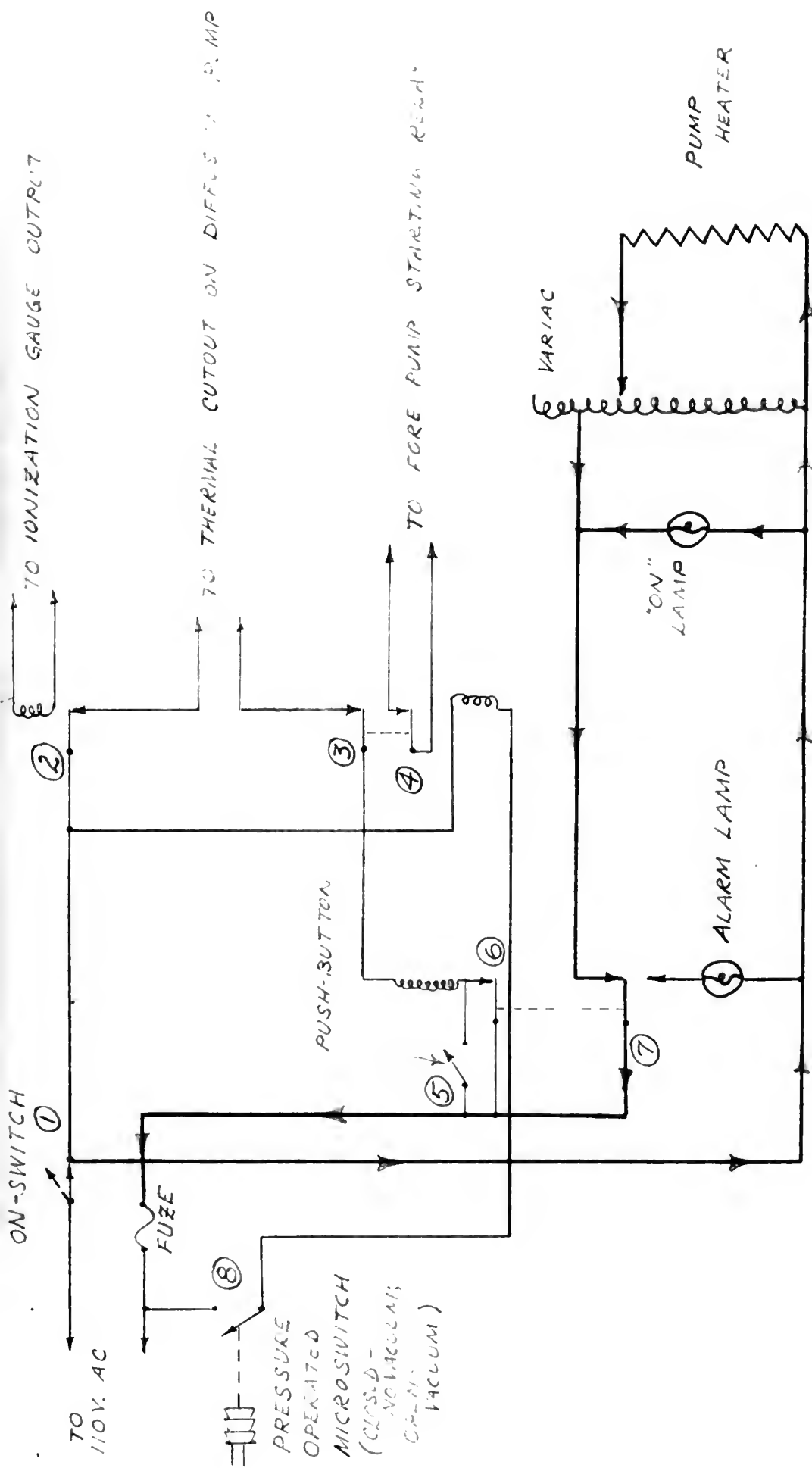


FIGURE 6
PUMP SAFETY INTERLOCK
CIRCUIT

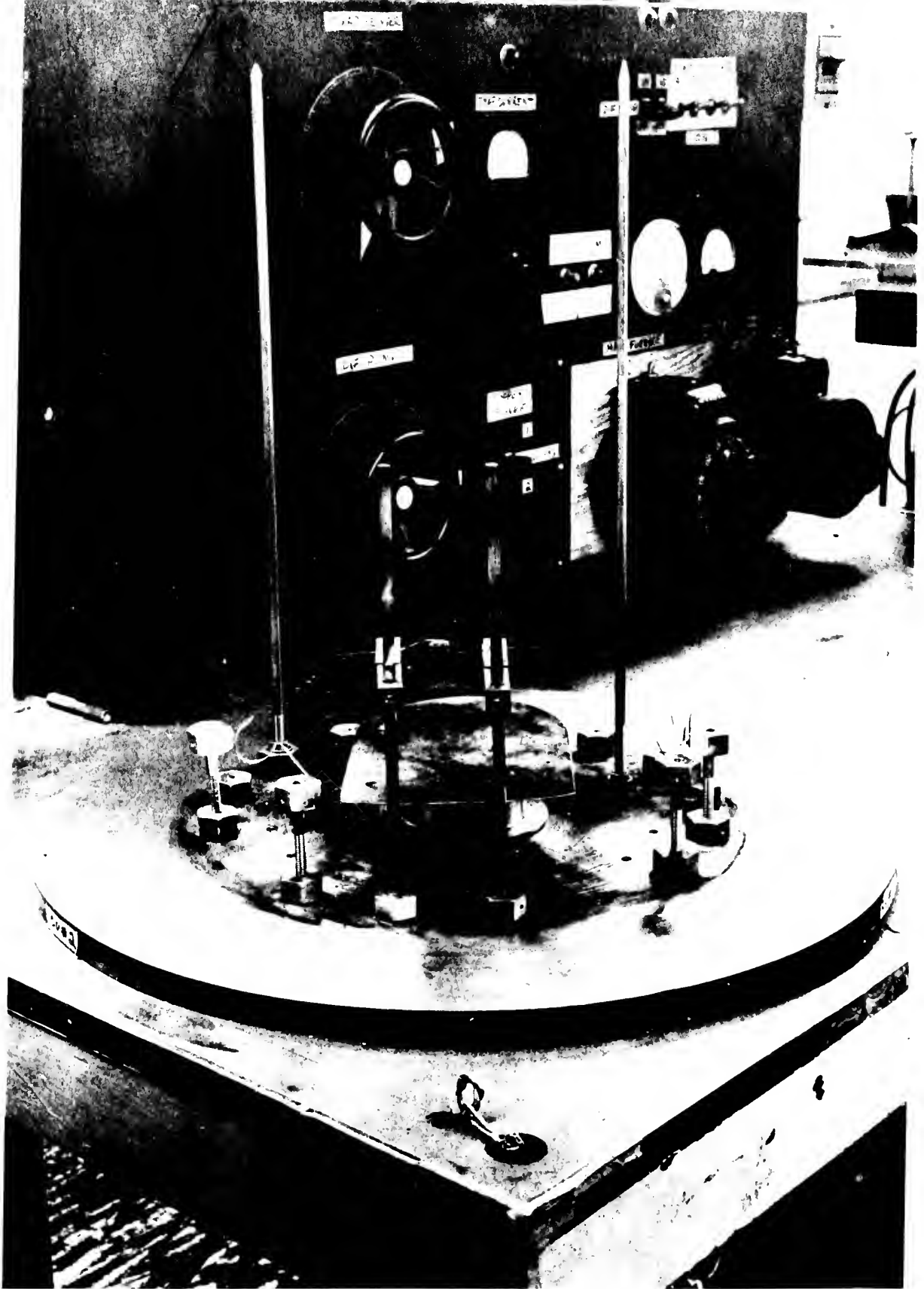


FIGURE 17
THE FINE POINT

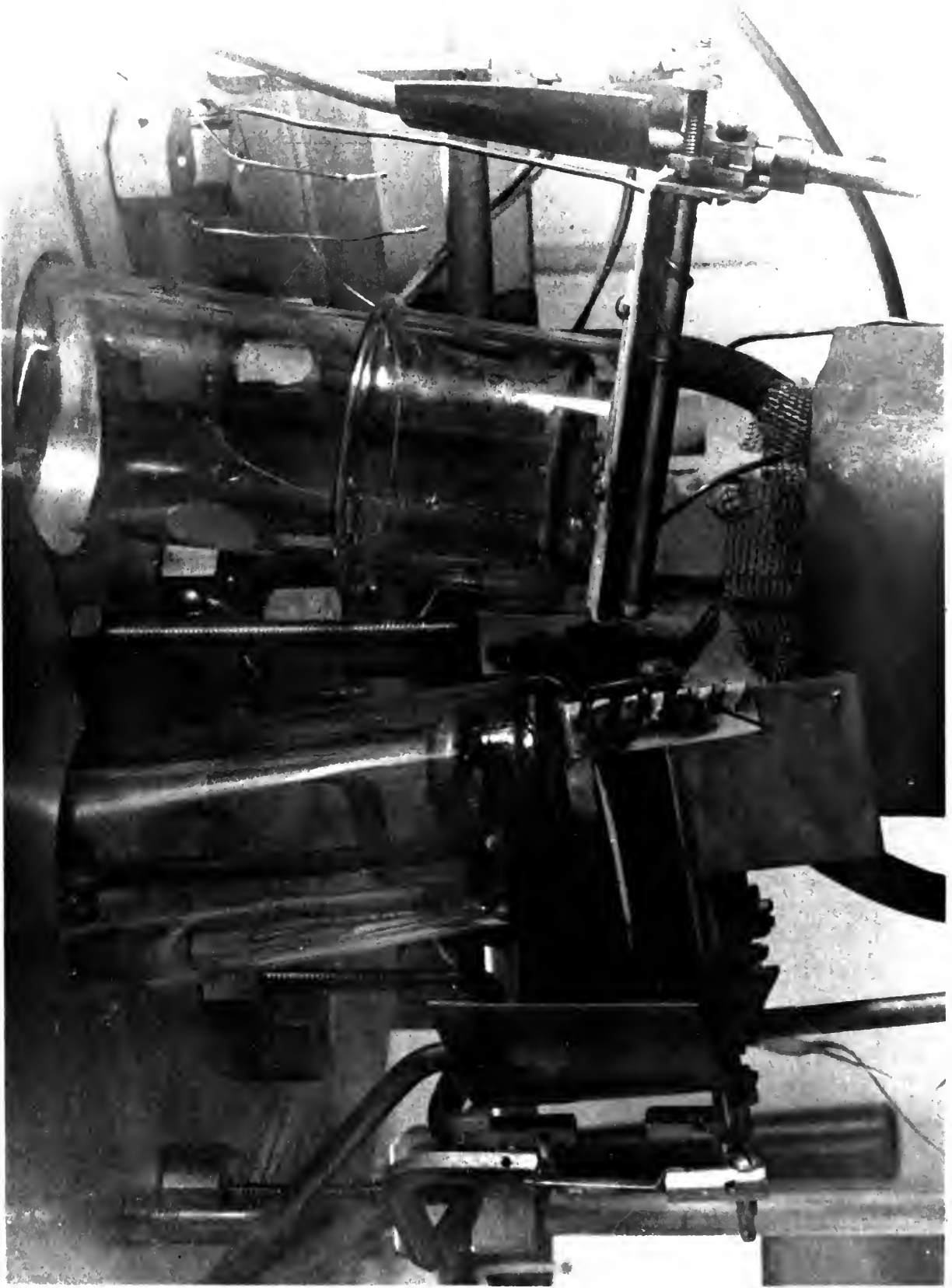


FIGURE 8
THE BEAKERS AND SHUTTER ASSEMBLY

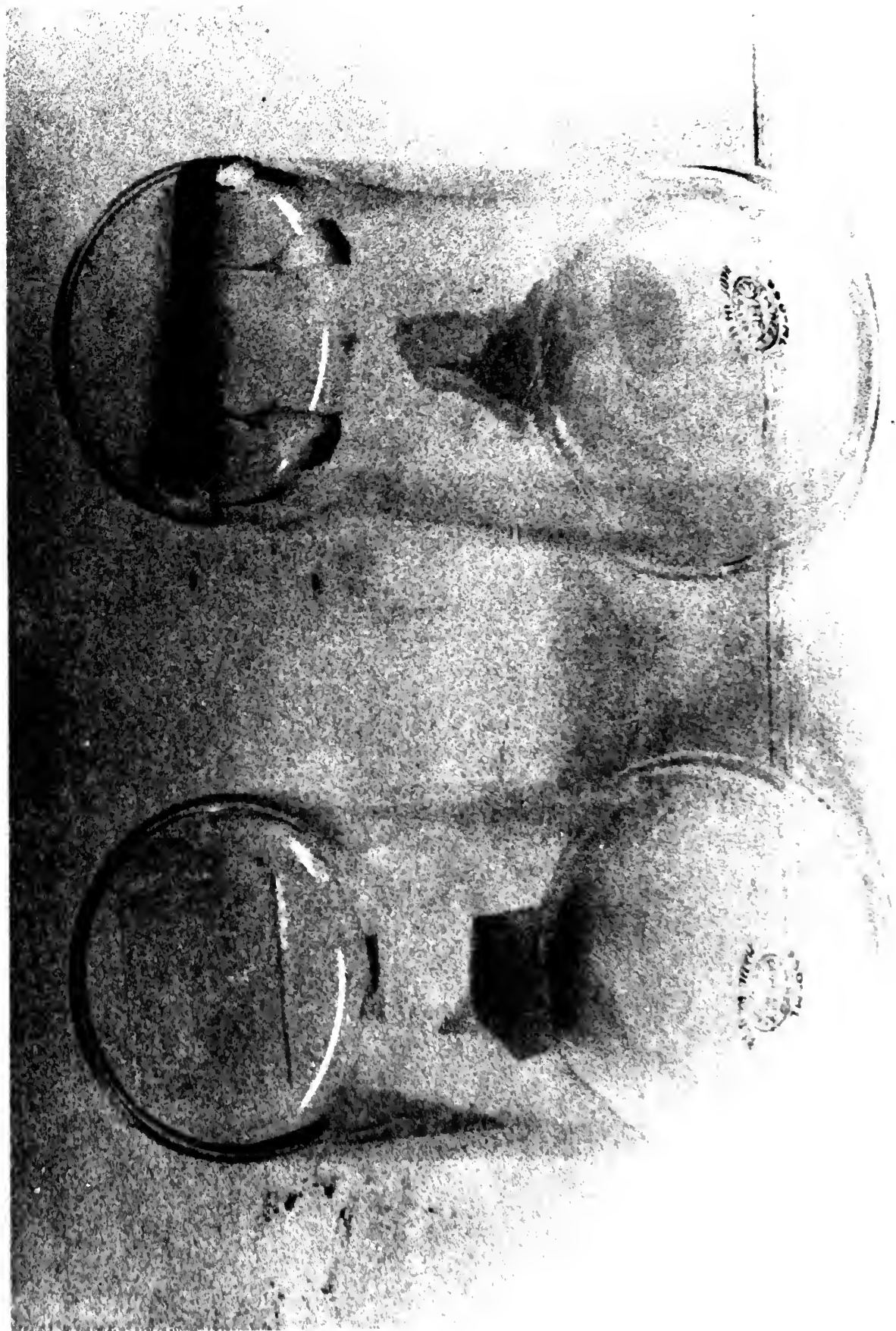


FIGURE 9
THE BEARERS

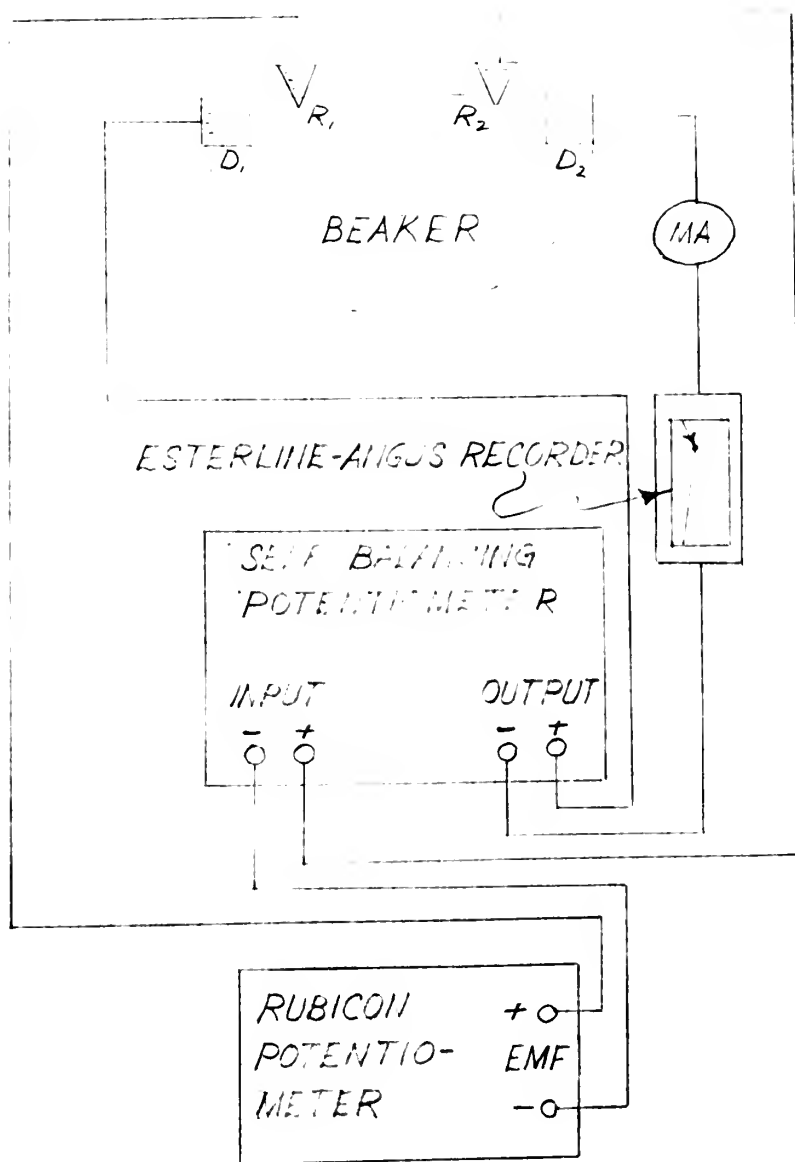
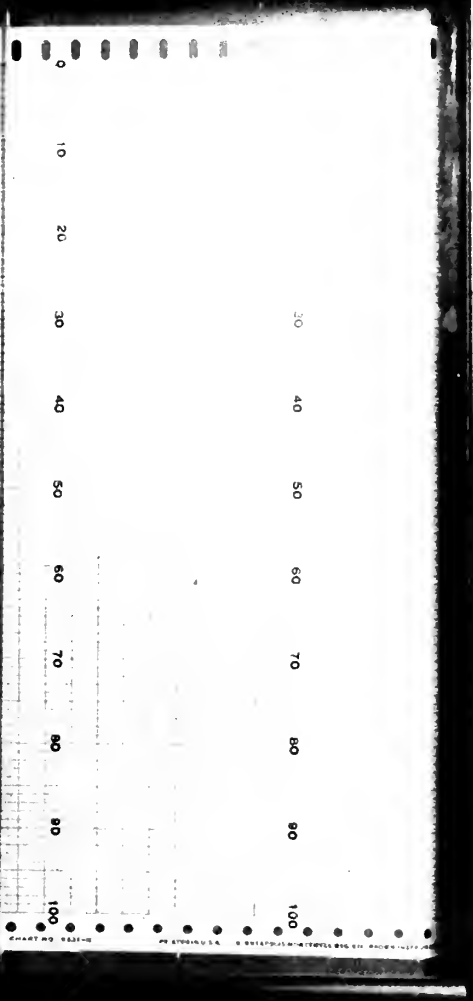


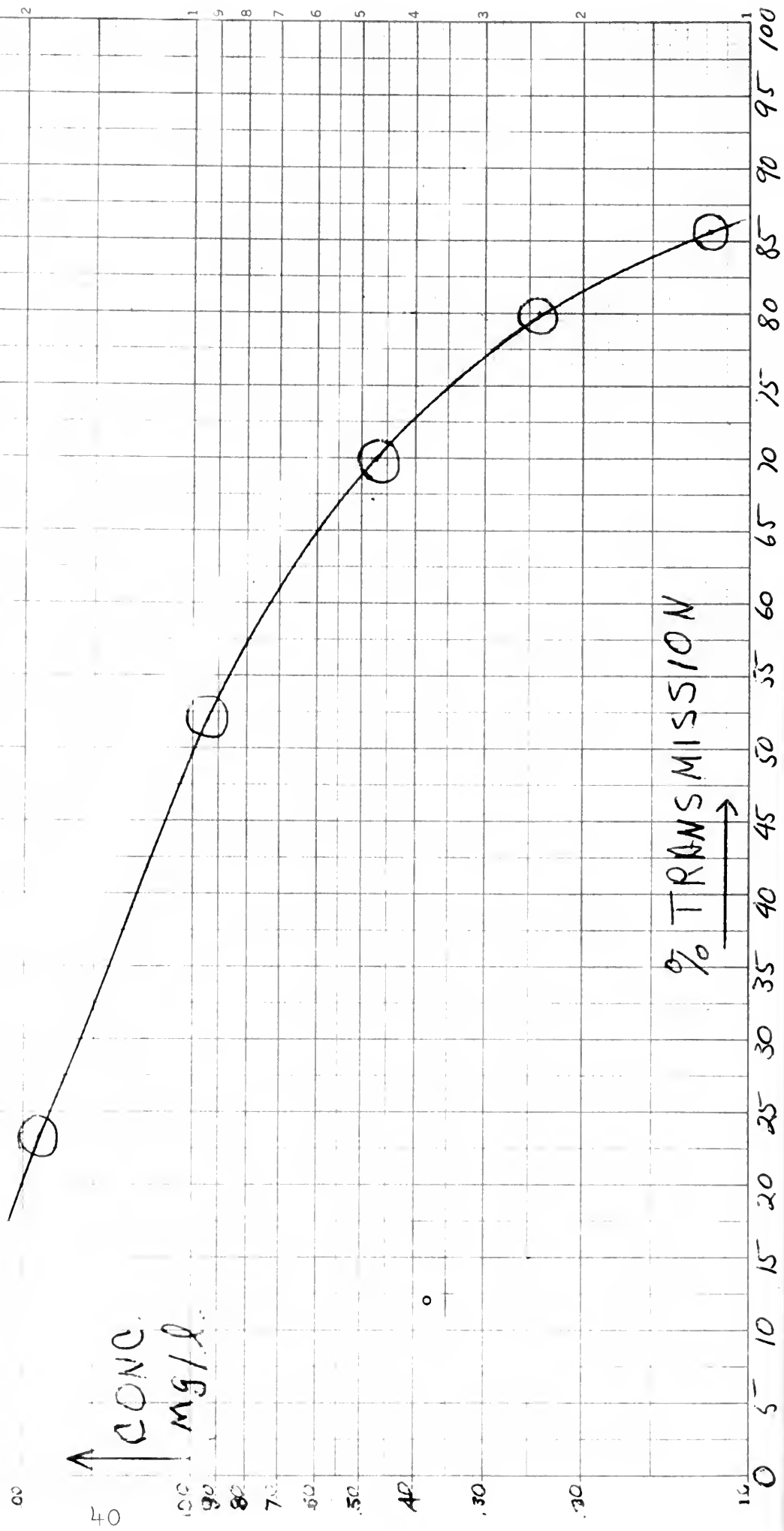
FIGURE 10
CONDUCTIVITY RECORDING CIRCUIT



CALIBRATION CURVE FOR IRON-CONSTANTAN THERMOCOUPLE

- Tabular points
- △ Exp. points
- corrected points





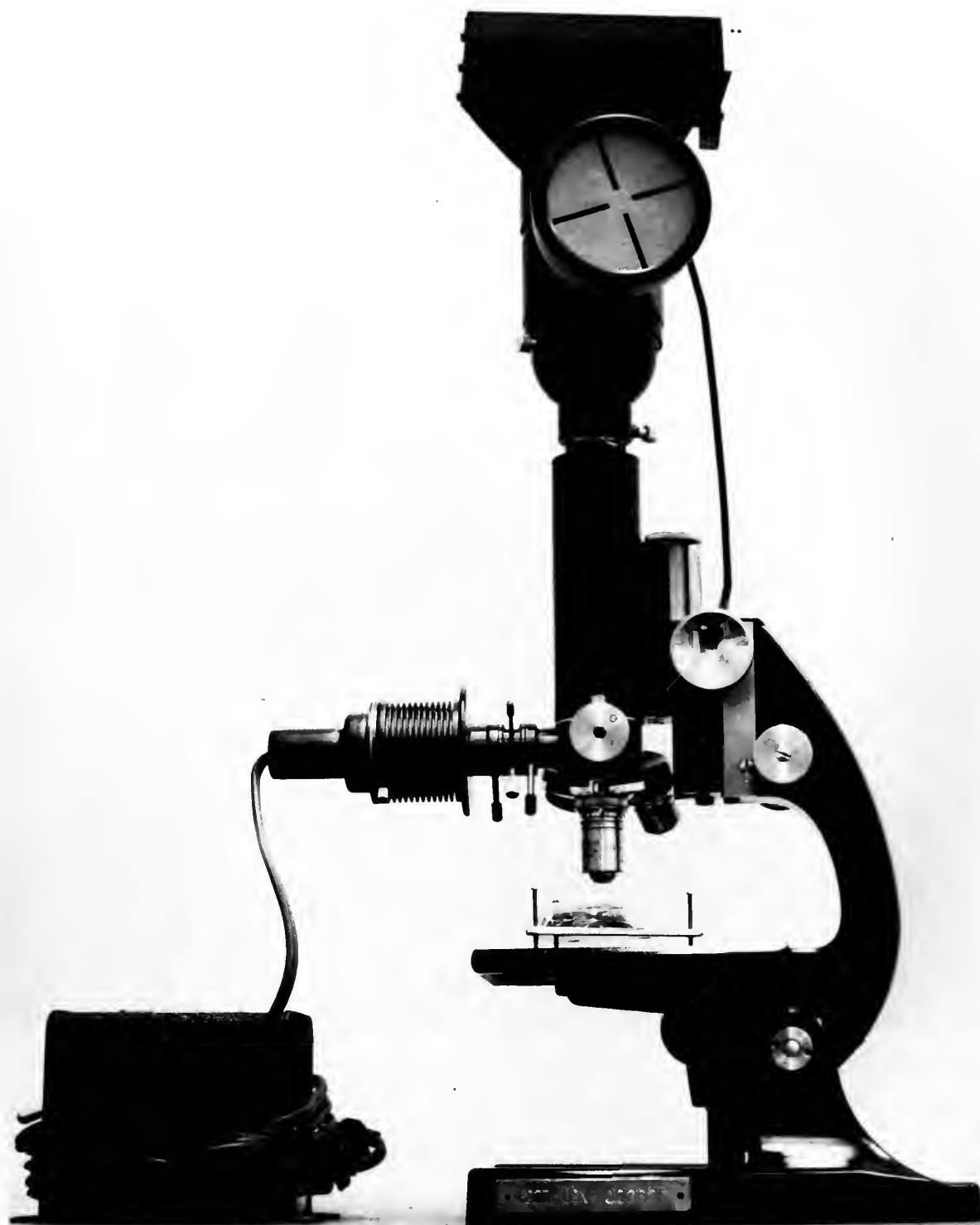


FIGURE 14
MICROSCOPE WITH CAMERA ATTACHMENT



FIGURE 15
SPECIFIC CRYSTALS

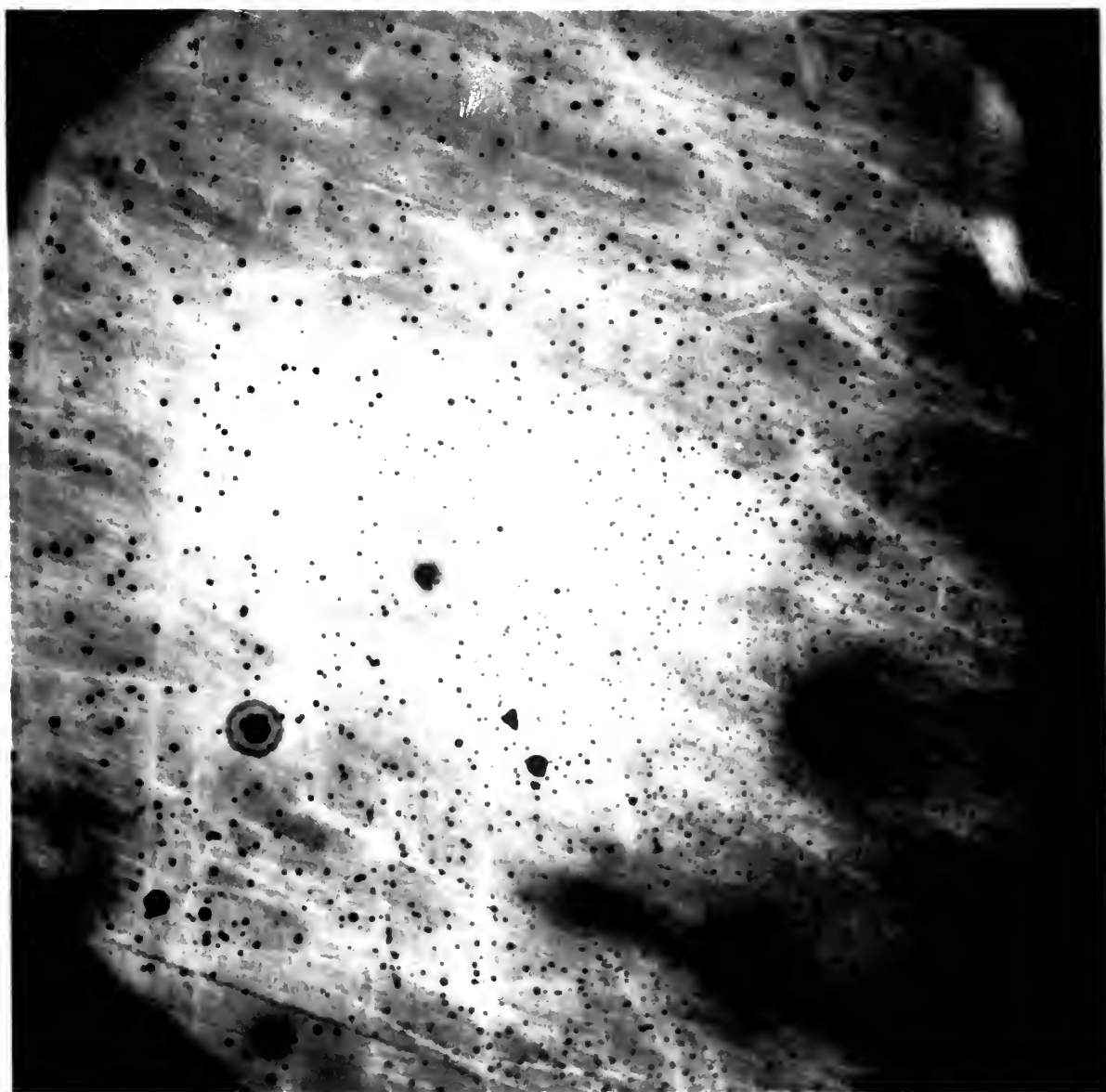


FIGURE 16
SPECIMEN CRYSTALS

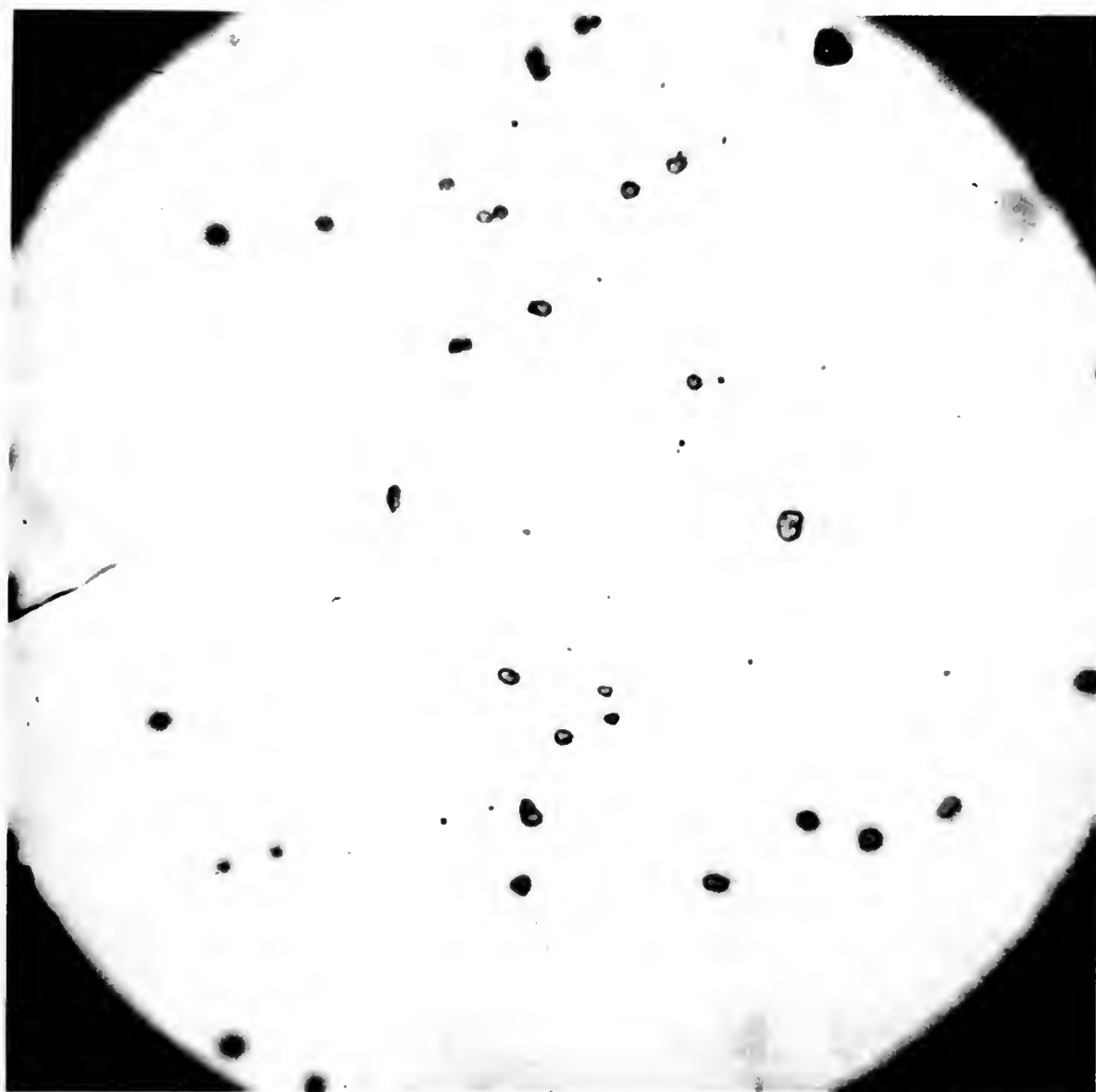


FIGURE 17
SPECIMEN CRYSTALS

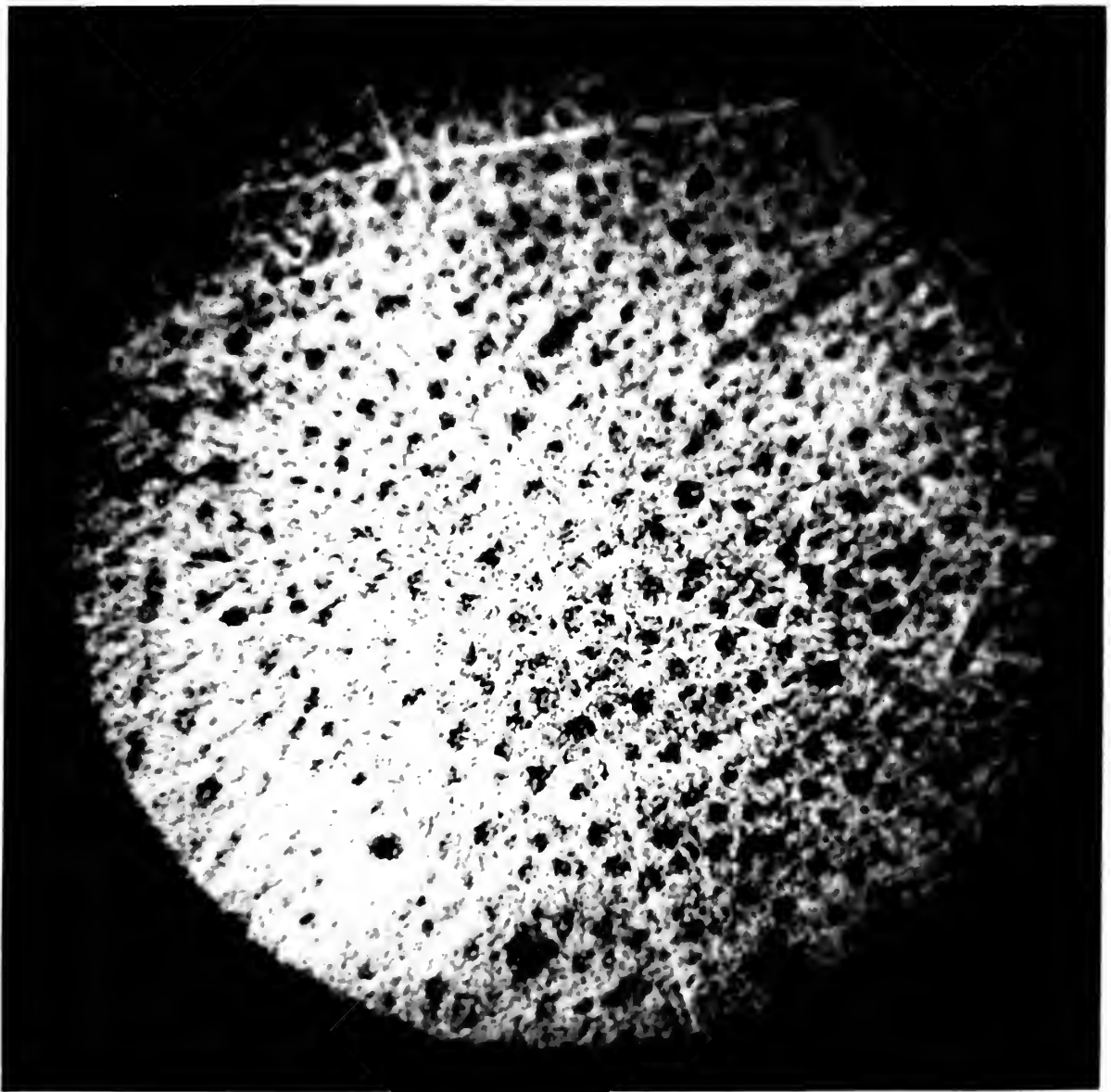


FIGURE 18
SPECIMEN CRYSTALS

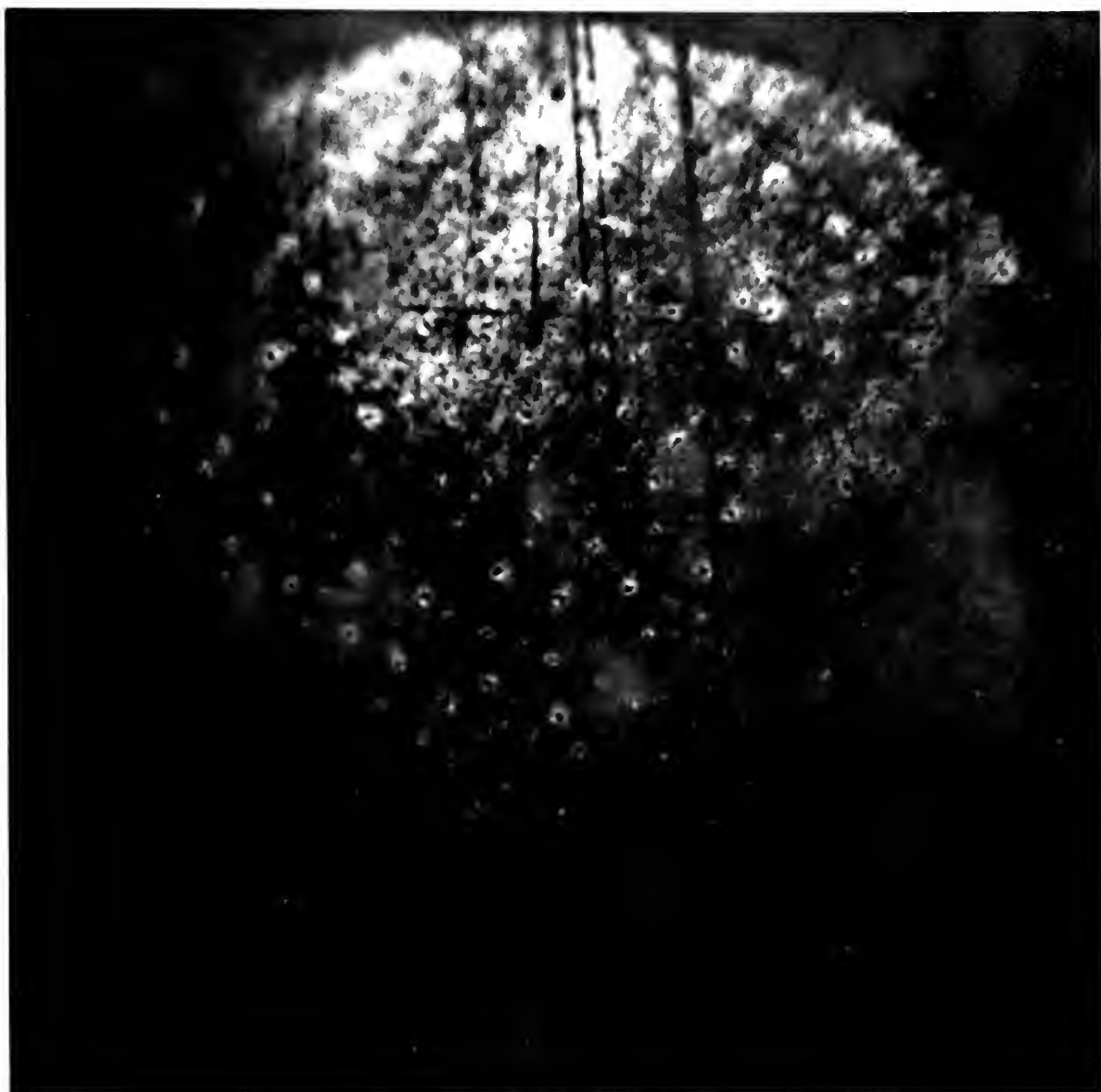


FIG. 1. 2
311. 1. 1. 1. 1. 1.



FIGURE 20
SPECIMEN CRYSTALS

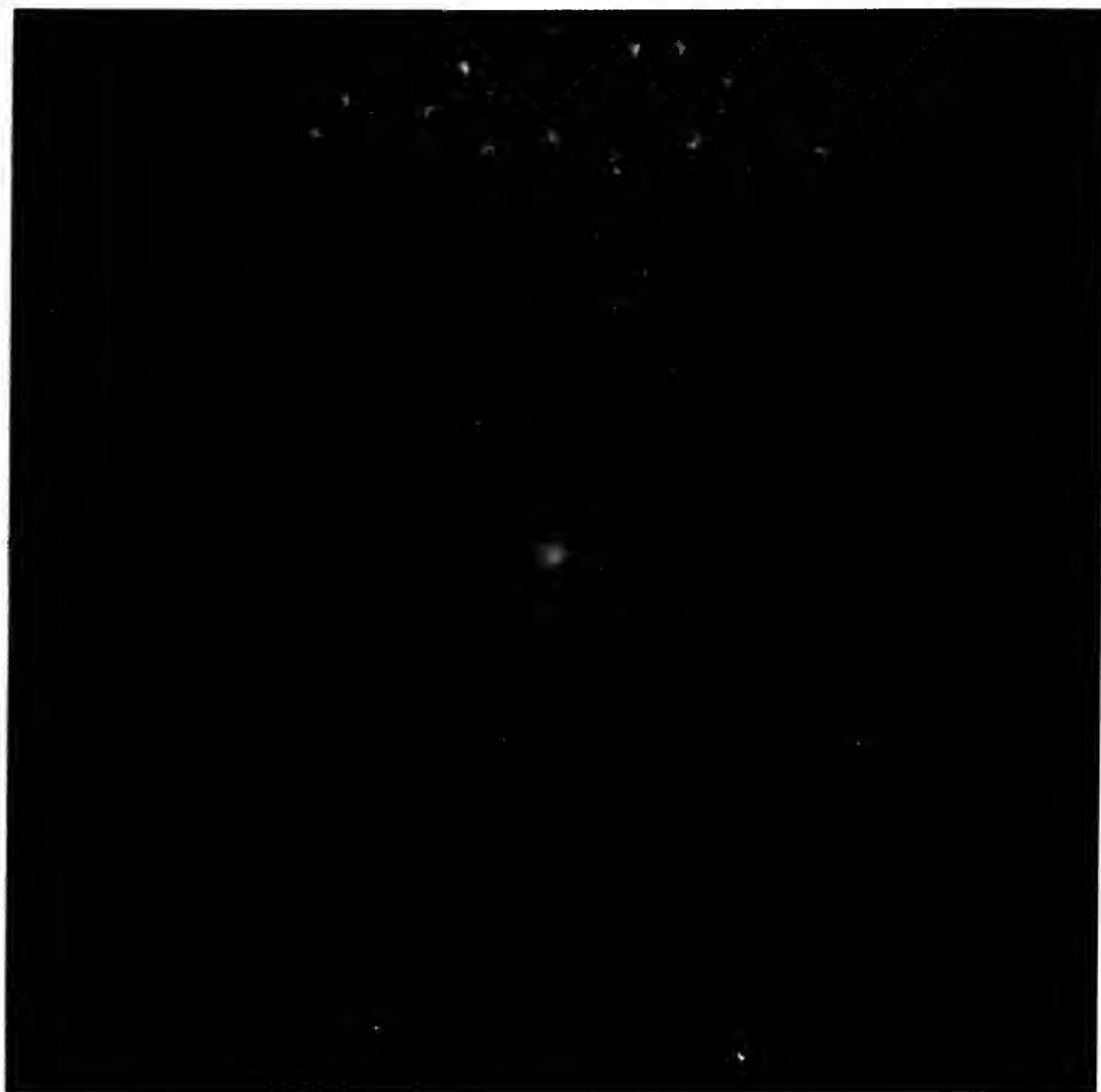


FIGURE 21
SPECIMEN CRYSTAL.

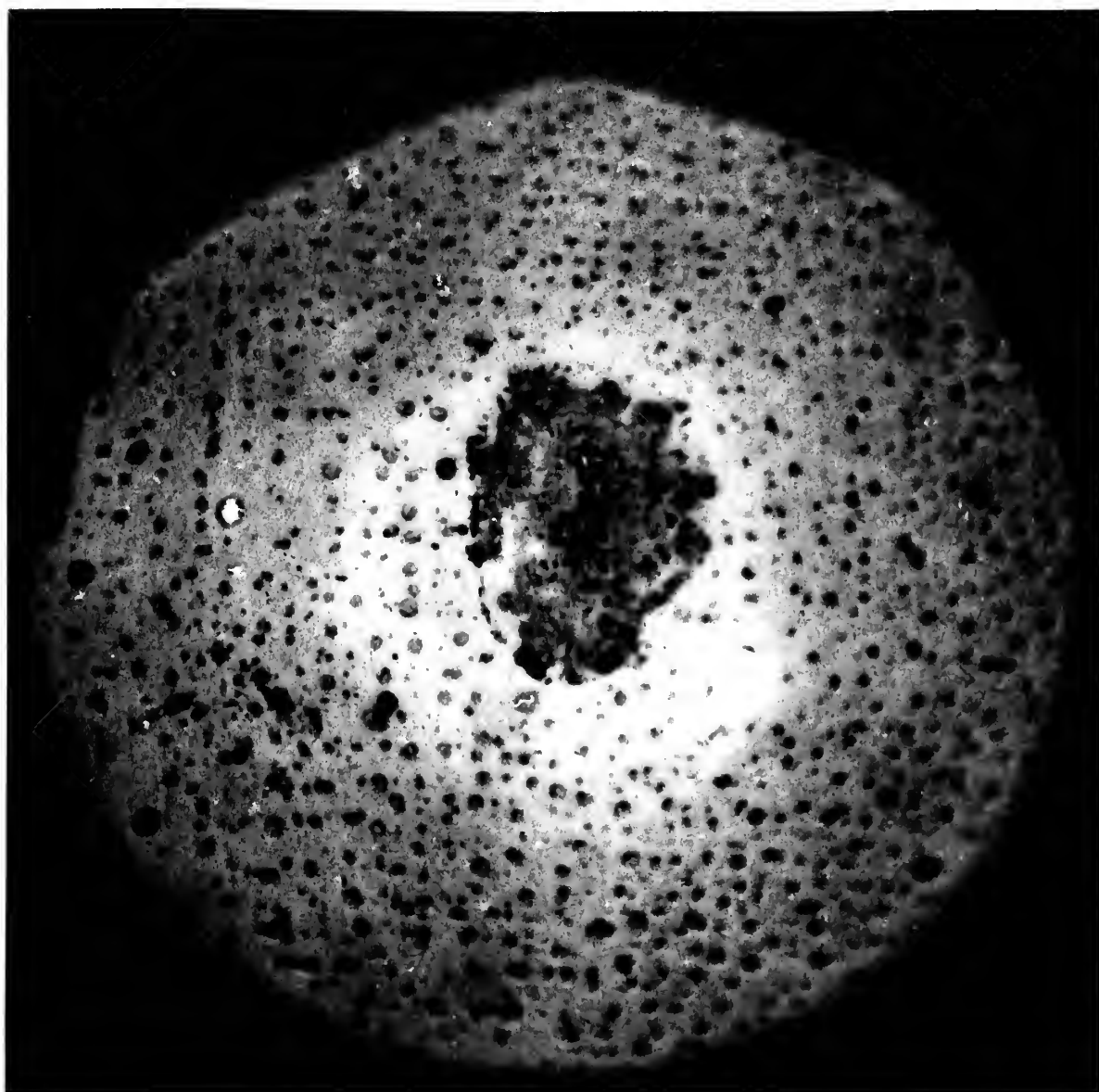


FIG. 5. 22
SPECIMEN CRYSTAL 3

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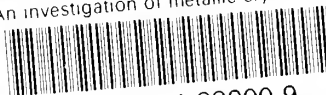
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